

# **A Review on Biomass Torrefaction Process and Product Properties**

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## **A Review on Biomass Torrefaction Process and Product Properties**

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### **Introduction**

Biomass Torrefaction is gaining attention as an important preprocessing step to improve the quality of biomass in terms of physical properties and chemical composition. Torrefaction is the slow heating of biomass in an inert or reduced environment to a maximum temperature of approximately 300°C. Torrefaction can also be defined as a group of products resulting from the partially controlled and isothermal pyrolysis of biomass occurring in a temperature range of 200–280°C. Thus, the process can be called a mild pyrolysis as it occurs at the lower temperature range of the pyrolysis process. At the end of the torrefaction process, a solid uniform product with lower moisture content and higher energy content than raw biomass is produced. Most of the smoke-producing compounds and other volatiles are removed during torrefaction, which produces a final product that has a lower mass but a higher heating value.

The present review looks into a) the torrefaction process and different products produced during the process and b) the solid torrefied material properties which include i) physical properties like moisture content, density, grindability, particle size distribution and particle surface area and pelletability ii) chemical properties like proximate and ultimate composition and iii) storage properties like off-gassing and spontaneous combustion.

### **Torrefaction Process Technique**

The thermochemical process of torrefaction is actually an incomplete pyrolysis process, and is characterized by the following parameters: reaction temperature 200–300°C, heating rate < 50°C/min, absence of oxygen, residence time < 30 minutes, ambient pressure, and flexible feedstock. Absence of oxygen in the reactor is of great importance to avoid oxidation and ignition (IEA, 2010).

### ***Biomass Reactions***

The cell in woody biomass is a rather complex construction of several building blocks. Polysaccharides are arranged in long chains called microfibrils enclosed in even structures of amorphous lignin and building the core of the crystalline cellulose. The cellulose is encased in a shell of hemicellulose. All these building blocks are more or less influenced by heat, but in different temperature ranges; therefore, they are

converted by specific reactions. The physiochemical changes in biomass during torrefaction are shown in Figure 1.

### Process Reactions

Drying: up to 200°C

Torrefaction reactions: 200–300°C

- Devolatilization and carbonization of hemicellulose
- Depolymerization and devolatilization/softening of lignin
- Depolymerization and devolatilization of cellulose.

### Process Results

Mass yield: ~70%

Energy yield: ~90%

Net calorific value change: (LHV) 17–19 MJ/kg → 18–23 MJ/kg

Moisture content: 1–2%

Hydrophobic, max: 1–6% moisture uptake.

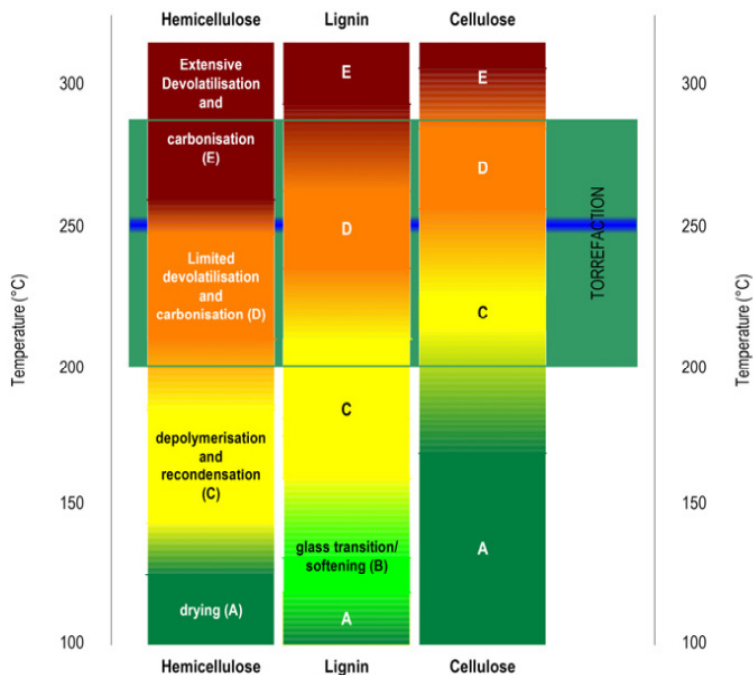


Figure 1. Physiochemical changes in biomass during torrefaction (Bergman et al., 2005a).

### Torrefaction products

Torrefaction is a mild pyrolysis process carried out at temperatures 200–300°C, in which biomass produces mainly three products: a solid product of a brown/dark color; a condensable liquid including mostly water, acetic acid, and other oxygenates; and non-condensable gases—mainly CO<sub>2</sub>, CO, and small amounts of methane. The last two products are categorized as volatiles. During torrefaction the raw material loses most of its moisture and other volatiles which have a low heat value. The type and amount of

gas that is released during torrefaction depends on the raw material type and torrefaction process conditions, including temperature and residence time.

## Composition of off-gas products produced during torrefaction

During torrefaction, numerous reaction products are formed. Their yield strongly depends on torrefaction conditions (temperature and time) and on biomass properties. Figure 2 (Bergman et al., 2005) gives an overview of the torrefaction products, classified based on their state at room temperature, which can be solid, liquid, or gas. The solid phase consists of a chaotic structure of the original sugars and reaction products. The gas phase includes the gases that are considered permanent, but also contains light aromatic components such as benzene and toluene. The condensables, or liquids, can be divided into three subgroups which include water, organics, and lipids (Figure 2). Reaction water from the water subgroup is a product of thermal decomposition. This liquid also contains free and bound water that has been released from the biomass by evaporation. The organics subgroup (in liquid form) consists of organics mainly produced during devolatilization and carbonization. Finally, the lipids subgroup contains compounds such as waxes and fatty acids that are present in the original biomass.

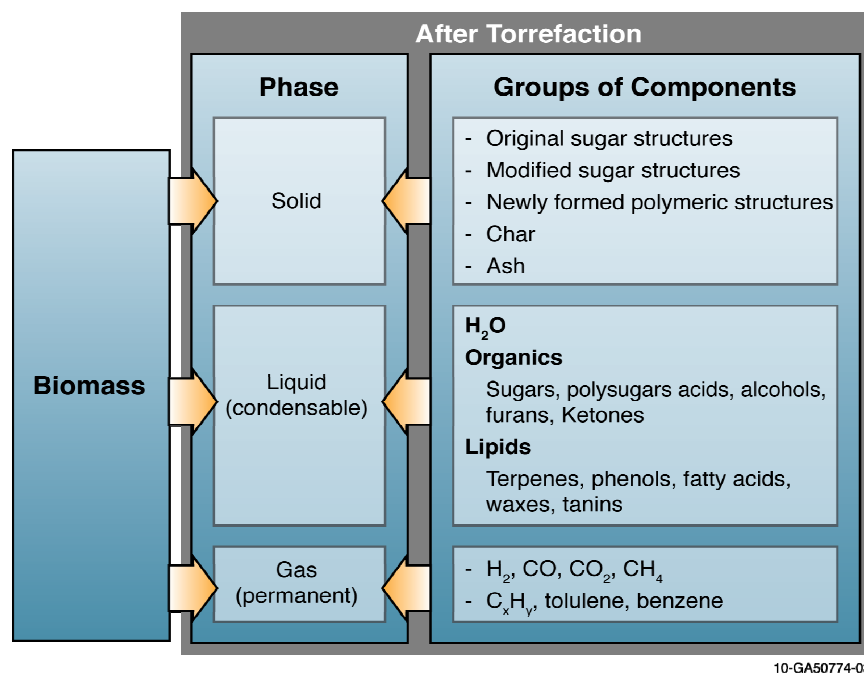


Figure 2. Products formed during torrefaction of biomass (Bergman et al. 2005).

### Condensable products

Water is the major condensable product. Water is released during drying due to evaporation and dehydration reactions between organic molecules. Acetic acid is also a condensable torrefaction product, mainly originating from acetoxy- and methoxy-groups present as side chains in xylose units present in the hemicelluloses fraction. Prins et al. (2006) showed that smaller quantities of formic acid, lactic acid, furfural, hydroxyl acetone, and traces of phenol are also present in the volatile component liberated

during the decomposition of biomass. For most of the condensable volatiles, their yields will increase with the torrefaction temperature, as shown in Figure 3. As a result, more energy is transferred to the volatiles fraction in the form of combustibles such as methanol and acetic acid.

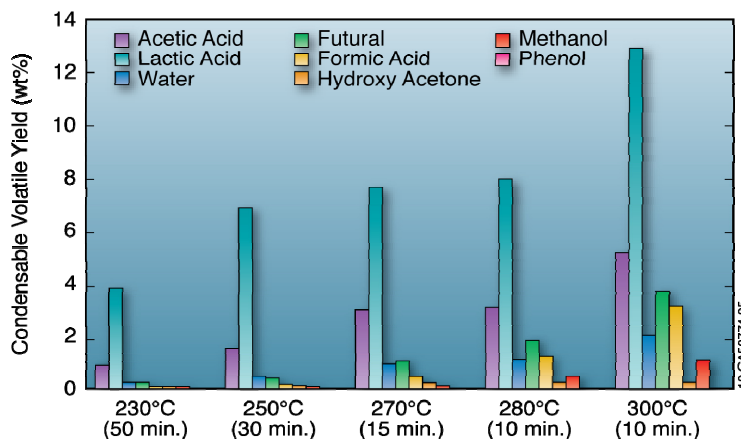


Figure 3. Product yields of condensable volatiles formed in torrefaction (Prins et al. 2006a).

### ***Non-condensable products***

The major gases formed in torrefaction are carbon dioxide and carbon monoxide, with only traces of other gases, as shown in Figure 4 (Bergman et al., 2005). Carbon monoxide (CO) is the main source of calorific value of the non-condensable torrefaction products.

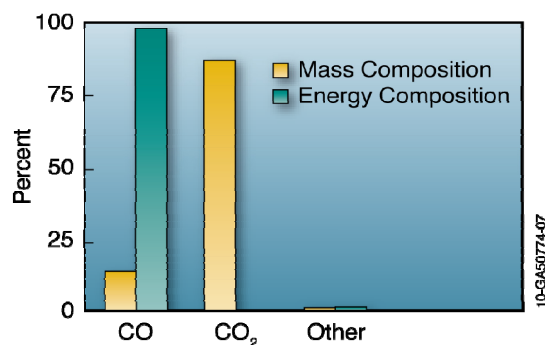


Figure 4. Compositions of the main permanent gases (Kiel, 2007).

The formation of CO<sub>2</sub> may be explained by decarboxylation of acid groups in the wood. The formation of CO cannot be explained by dehydration or decarboxylation reactions. The increased CO formation is reported as the reaction of carbon dioxide and steam with porous char (White and Dietenberger, 2001). Traces of hydrogen and methane is also detected in the non-condensable products. A gas composition comparison between wood and agricultural residues indicates that the latter is characterized by a higher CO<sub>2</sub> production (Bergman et al., 2005; Prins et al., 2006; Deng et al., 2009). In addition, a kinetic study on the generation of non-condensable gases shows that the gases are formed through parallel independent first-order reactions (Prins et al., 2006). The ratio

of CO to CO<sub>2</sub> increased with temperature because cellulose and lignin decompose at higher temperatures (Prins et al., 2006).

## Physical properties of Solid Torrefied Biomass

Torrefaction of biomass significantly changes physical properties like moisture content, density, grindability, pelletability, hydrophobicity, and calorific value, (Sadaka and Negi, 2009) and the chemical composition in terms of carbon, hydrogen, oxygen, nitrogen and sulfur.

### Moisture content

Being a deep drying process, torrefaction reduces the moisture content of the pre-dried biomass from 10% to <6% (Lipinsky et al., 2002). Typically the moisture content of torrefied biomass ranges between 1–6% on a weight basis, depending on torrefaction conditions (Bergman and Kiel, 2005). Some studies conducted by Tumuluru et al. (2010) on torrefaction of corn stover using a bubbling sand bed indicated that the moisture content was between 1-2% when torrefaction temperatures and residence times are >300°C and >30 min (Fig. 3). They have also developed a regression equation (Eq. 1) to predict the changes in moisture content with respect to torrefaction temperature and time in the range of 250-350°C and 30-120 min. The same authors made similar observations while torrefying miscanthus samples. Sadaka and Negi's (2009) in their studies on torrefaction of wheat straw, rice straw, and cotton gin waste at 200, 260, and 315°C for 60, 120, and 180 minutes has concluded that there is a significant reduction of moisture content at the extreme conditions (315°C for 180) for all three feedstock's by 70.5, 49.4, and 48.6%.

### Density

Mass loss in the form of solids, liquids, and gases during the torrefaction process causes the biomass to become more porous. This results in a significant reduction in volumetric density, typically between 180–300 kg/m<sup>3</sup>, depending on initial biomass density and torrefaction conditions (Bergman and Kiel, 2005). Rodrigues and Rousset (2009), in their studies on the effect of torrefaction on energy properties of *Eucalyptus grandis* wood, indicated that there is a loss of 14.12% of bulk density when it is torrefied at 280°C for 30 minutes. Table 1 indicates the loss of bulk density at torrefaction temperatures ranging 220–280°C.

Table 1. Bulk density (dry basis) of torrefied *Eucalyptus grandis* wood.

Treatment	Bulk density (g/cm <sup>3</sup> )	Percentage loss
Control*	0.85 <sup>a</sup>	–
T2-220°C	0.83 <sup>a</sup>	2.35
T3-250°C	0.79 <sup>b</sup>	7.06
T4-280°C	0.73 <sup>c</sup>	14.12

Note: Means followed by the same letter in the superscript are statistically similar at the 5% probability level. \* Average moisture content of control treatment = 15%.



## **Grindability**

Biomass is highly fibrous and tenacious in nature, because fibers form links between particles and make the handling of raw ground samples difficult. During the torrefaction process the biomass loses its tenacious nature, which is mainly coupled to the breakdown of the hemicellulose matrix and depolymerization of the cellulose, resulting in the decrease of fiber length (Bergman et al., 2005; Bergman and Kiel, 2005). The decrease in particle length, but not in diameter per se, results in better grindability, handling characteristics, and flowability through processing and transportation systems. During the torrefaction process the biomass tends to shrink; become lightweight, flaky, and fragile; and lose its mechanical strength, making it easier to grind and pulverize (Arias et al., 2008). Bergman and Kiel (2005) conducted studies on the energy requirements for grinding raw and torrefied biomass like willow, woodcuttings, demolition wood, and coal using a heavy duty cutting mill. They concluded that power consumption reduces dramatically, from 70–90%, based on the conditions under which the material is torrefied. They have also found that the capacity of the mill increases by a factor 7.5–15. The most important phenomenon they observed was that the size reduction characteristics of torrefied biomass resulted in a similar product as coal.

## **Particle size distribution, sphericity, and particle surface area**

Particle size distribution curves, sphericity, and surface area are important parameters for understanding flowability and combustion behavior during cofiring. Many researchers observed that ground, torrefied biomass produced narrower, more uniform particle sizes compared to untreated biomass due to its brittle nature, which is similar to coal. Phanphanich and Mani (2011) study on torrefied pine chips and logging residues found that smaller particle sizes are produced compared to untreated biomass. They have also observed that the particle distribution curve was skewed towards smaller particle sizes with increased torrefaction temperatures.

Torrefaction also significantly influences the sphericity and particle surface area. Phanphanich and Mani (2011) results also indicated that sphericity and particle surface area increases as the torrefaction temperature was increased to 300°C. For ground, torrefied chips, they found that the sphericity increased from 0.48–0.62%, concluding that an increase in particle surface area or decrease in particle size of torrefied biomass can be desirable properties for efficient cofiring and combustion applications. Also, the bulk and particle densities of ground torrefied biomass increases as it reduces the inter and intra particle voids generated after milling (Esteban and Carrasco, 2006). Studies have indicated that ground torrefied material results in a powder with a favorable size distribution and sphericity, allowing it to meet the smooth fluidization regime required for feeding it to entrained-flow processes (gasifier and pulverized coal).

## **Pelletability**

Torrefying the biomass before pelletization produces uniform feedstock with consistent quality. Densification following torrefaction is considered by several researchers (Lipinsky et al., 2002; Reed and Bryant, 1978 and Bergman et al., 2005). These studies indicated that the pressure required for densification can be reduced by a factor of two when material is densified at a temperature of 225°C and the energy consumption

during densification is reduced by a factor of two compared to raw biomass pelletization using a pellet mill. Densification experiments were carried out on untreated and torrefied biomass using a piston press (Pronto-Press), which can be operated at different pressures and temperatures, to understand the densification behavior of different types of torrefied biomass. The pellets produced based on the TOP process had higher bulk densities, in the range of 750–850 kg/m<sup>3</sup>, with relatively high-calorific value (LHV basis), generally 19–22 MJ/kg. The energy density of TOP pellets ranged from 15–18.5 GJ/m<sup>3</sup> and is comparable to subbituminous coal, which typically has a value of 21–22 GJ/m<sup>3</sup>. The pellets produced had a higher mechanical strength, typically 1.5–2 times greater, than the conventional pellets. The higher mechanical strength of these pellets is due to densification of the biomass at high temperature, which causes the biomass polymers to be in a weakened state (less fibrous, more plastic). Higher durable pellets from torrefied biomass can be due to chemical modifications, occurring during torrefaction, that lead to more fatty structures that act as binding agent. In addition, the lignin content increases by 10–15%, as the devolatilization process predominantly concerns hemicellulose (Bergman, 2005). Figure 5 shows the flow diagram for the torrefaction and pelletization (TOP) process that Bergman (2005) proposed.

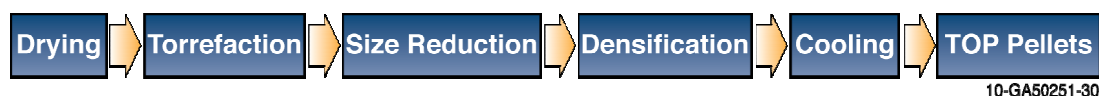


Figure 5. Flow diagram for production of torrefied wood pellets.

## Chemical composition of the torrefied biomass

Besides improving physical attributes, torrefaction also results in significant changes in proximate and ultimate composition of biomass and makes it more suitable for fuel applications. Sadaka and Negi's (2009) study on torrefaction of wheat straw, rice straw, and cotton gin waste at 200, 260, and 315°C for 60, 120, and 180 minutes concluded that moisture content was reduced at the extreme conditions (315°C for 180) for all three feedstock's by 70.5, 49.4, and 48.6%, and the heating value increased by 15.3, 16.9, and 6.3%, respectively. Zanzi et al. (2002), in their study on miscanthus torrefaction made similar observations, where increasing temperature from 230–280°C and time from 1–3 hours increased the carbon content and decreased the hydrogen, nitrogen, and oxygen content. At 280°C, the carbon content increased to about 52% from an initial value of 43.5% while hydrogen and nitrogen content decreased from 6.49–5.54% and 0.90–0.65% for 2 hours of torrefaction. In general, increased torrefaction temperatures result in increased carbon content and decreased hydrogen and oxygen content due to the formation of water, CO, and CO<sub>2</sub>. This process also causes the hydrogen-to-carbon (H/C) and oxygen-to-carbon (O/C) ratios to decrease with increasing torrefaction temperature and time, which results in less smoke and water-vapor formation and reduced energy loss during combustion and gasification processes. In torrefaction studies of reed canary grass and wheat straw torrefaction at 230, 250, 270, and 290°C for 30-minute residence times, Bridgeman et al. (2008) found that the moisture content decreases from an initial value of 4.7%–0.8%. They found that



carbon increased 48.6–54.3%, and hydrogen and nitrogen content decreased from 6.8–6.1% and 0.3–0.1%, respectively. Bridgeman et al. (2010) in their studies on torrefaction of willow and miscanthus indicated that at higher temperatures and residence times, the atomic O: C and H: C ratios are closer to that of lignite coal. Table 6 shows the effect of different torrefaction temperatures on ultimate compositional changes in woody and herbaceous biomass. Table 2 and 3 indicates the elemental composition of the torrefied biomass at different temperatures and times.

Table 2. Elemental compositions of solid products.

Biomass	Temperature (°C)	Time (h)	C	H	N	O
	Moisture and ash free (wt, %)					
Birch	Raw		47.40	6.11	0.16	46.33
	230	1	48.20	5.93	0.16	45.71
	230	2	48.72	5.88	0.14	45.26
	230	3	48.82	5.76	0.13	45.29
	250	1	49.50	5.69	0.13	44.68
	250	2	49.86	5.68	0.12	44.34
	250	3	50.05	5.65	0.12	44.18
	280	1	51.25	5.63	0.11	43.01
	280	2	52.00	5.62	0.11	42.27
	280	3	52.50	5.62	0.11	41.77

Source: Zanzi et al. (2002).

Table 3. Ultimate analysis of biomass solid.

Biomass solid	Temperature (°C)	C	H	N	S	O
Loblolly Pine	n/a	50.25	5.97	0	0	43.34
Wet torrefied loblolly pine	200	54.72	6.03	0.14	0	39.11
	230	56.05	5.94	0.09	0	37.92
	260	72.07	4.90	0.16	0	22.89

Source: Yan et al. (2010).

## Storage aspects of torrefied biomass

### Off-gassing

Storage issues like off-gassing and self-heating may also be insignificant in torrefied biomass as most of the solid, liquid, and gaseous products that are chemically and microbiologically active are removed during the torrefaction process. Kuang et al. (2009) and Tumuluru et al (2010) studies on wood pellets concluded that high storage temperatures of 50°C can result in high CO and CO<sub>2</sub> emissions, and the concentrations

of these off-gases can reach up to 6% for a 60-day storage period. These emissions were also found to be sensitive to relative humidity and product moisture content. The same researchers at University of British Columbia conducted studies on off-gassing from torrefied wood chips and indicated that CO and CO<sub>2</sub> emissions were very low; nearly one third's of the emissions from regular wood chips at room temperature (20°C). The reason could be due to low moisture content and reduced volatile content which could result in less reactivity with the storage environment.

Biomass is porous, often moist, and prone to off-gassing and self heating due to chemical oxidation and microbiological activity. In general, the biomass moisture content plays an important role in initiating chemical and microbial reactions. Moisture content coupled with high storage temperatures can cause severe off-gassing and self-heating from biomass-based fuels. Another important storage issue of ground torrefied biomass is its reactivity in powder form, which can result in fire during storage. It is preferred to store the torrefied biomass in an inert environment to avoid accidents due to spontaneous combustion. Kiel (2007) in his laboratory-scale combustion studies of torrefied wood found that it is highly reactive, similar to coal.

### ***Hydrophobicity***

An advantage of torrefied pellets over regular raw pellets is that they are hydrophobic (moisture uptake is almost negligible) even under severe storage conditions. In general, the uptake of water by raw biomass is due to the presence of OH groups. Torrefaction produces a hydrophobic product by destroying OH groups and causing the biomass to lose the capacity to form hydrogen bonds (Pastorova et al., 1993). Due to these chemical rearrangement reactions, non-polar unsaturated structures are formed, which preserve the biomass for a long time without biological degradation, similar to coal (Bergman and Kiel, 2005; Wooten et al., 2000).

Bergman (2005) determined the hydrophobicity of torrefied pellets by immersing them in water for 15 hours. The hydrophobic nature was evaluated based on the state of the pellet after this period and by gravimetric measurement to determine the degree of water uptake. Bergman (2005) study indicated that raw pellets swelled rapidly and disintegrated into original particles. Torrefied pellets produced under optimal conditions, however, did not disintegrate and showed little water uptake (7–20% on mass basis). He also concluded that torrefaction conditions play a vital role in the hydrophobic nature of biomass. Sokhansanj et al. (2010) compared the moisture uptake of the torrefied biomass to the untreated biomass and found that there is about a 25% decrease in the water uptake when compared to the control (Figure 6).

Table 4 shows, torrefied pellets properties with respect to wood, wood pellets, charcoal and coal. It is clear that the product characteristics of torrefied material like handling, milling, and transport requirements are similar to coal. In cofiring operations torrefied pellets allow for higher co-firing percentages up to 40% due to matching fuel properties with coal, and they can use the existing equipment setup for coal.

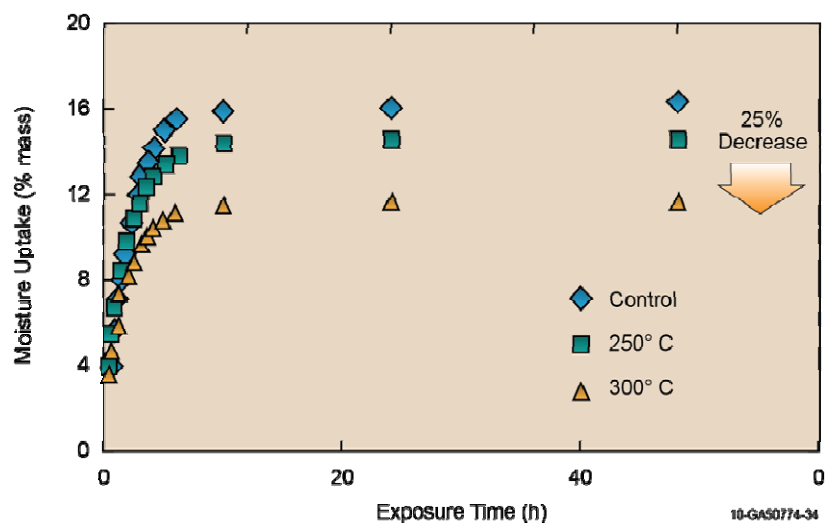


Figure 6. Moisture uptake by the torrefied wood pellets made from 0.8-mm particle size.

Table 4. Indicative properties of different biomass and coal based fuels (Kleinschmidt 2011).

Properties	Wood	Wood pellets	Torrefied pellets	Charcoal	Coal
Moisture content (% wt)	30–45	7–10	1–5	1–5	10–15
Calorific value (MJ/kg)	9–12	15–16	20–24	30–32	23–28
Volatiles (% db)	70–75	70–75	55–65	10–12	15–30
Fixed carbon (% bd)	20–25	20–25	28–35	85–87	50–55
Bulk density (kg/l)	0.2–0.25	0.55–0.75	0.75–0.85	~0.20	0.8–0.85
Volumetric energy density (GJ/m <sup>3</sup> )	2.0–3.0	7.5–10.4	15.0–18.7	6–6.4	18.4–23.8
Dust	Average	Limited	Limited	High	Limited
Hygroscopic properties	Hydrophilic	Hydrophilic	Hydrophobic	Hydrophobic	Hydrophobic
Biological degradation	Yes	Yes	No	No	No
Milling requirement	Special	Special	Classic	Classic	Classic

Handling requirements	Special	easy	Easy	Easy	Easy
Product consistency	Limited	High	High	High	High
Transport cost	High	Average	Low	Average	Low

## Torrefied biomass applications

Pulverized fuel combustion in coal-fired power stations and entrained flow gasification are particularly interesting product outlets for biomass. In both applications, biomass has to be fed to the reactor as a powder, which is difficult, costly, and achievable only at very low capacity in classical coal-mills. Due to this limitation, wood pellets are currently the state-of-the-art for co-firing, as they consist of sufficiently small particles.

Consequently, wood pellets also have some limitations in terms of energy content and moisture uptake during storage and transportation. Torrefied biomass being energy dense and hydrophobic in nature can be a good replacement for wood pellets in co-firing and gasification plants. The high fuel quality of torrefied biomass makes it very attractive for combustion and gasification applications. Due to high CVs, the thermal energies of the combustion and gasification system can be improved significantly (Bergman and Kiel, 2005). However, there is no data on milling, handling, storing, transporting, and combusting large amounts of torrefied biomass at a commercial scale. Other applications include (1) high-quality smokeless solid fuels for industrial, commercial, and domestic applications; (2) solid fuel for cofiring directly with pulverized coal at electric power plants; (3) an upgraded feedstock for fuel pellets, briquettes, and other densified biomass fuels; and (4) high quality biomass solid fuel for advanced bioenergy application.

## CONCLUSIONS

1. Torrefied biomass in general defines a group of products resulting from the partially controlled and isothermal pyrolysis of biomass occurring at a temperature range of 200–300°C.
2. The common torrefaction reactions include (a) devolatilization and carbonization of hemicelluloses and (b) depolymerization and devolatilization of lignin and cellulose.
3. Torrefaction reduces the variability in biomass feedstocks and helps to develop a uniform feedstock with consistent physical, chemical, and biochemical composition.
4. Torrefaction of biomass improves:
  - Physical properties like grindability and pelletability, thereby increasing energy density
  - Ultimate and proximate composition by increasing the carbon content and calorific value and decreasing the moisture and oxygen content

- Biochemical composition by decomposing the hemicelluloses and softening the lignin, resulting in better binding during pelletization.
5. Densification of torrefied material at 225°C reduces the energy consumption and increases the throughput by a factor of two.
  6. During torrefaction, the biomass loses most of the low energy content material (a) solids, which include original sugar structures and other newly formed polymeric structures; (b) liquids, which are condensables like water organics and lipids, and (c) gases like CO and CO<sub>2</sub>.
  7. Off-gas emissions from a torrefied biomass during storage are less when compared to raw biomass.
  8. Torrefied biomass, being hydrophobic, does not absorb moisture from the environment and remains stable for long storage times.
  9. Torrefied biomass has a wider range of application, especially when densified and used in power generation plants along with coal.

## ACKNOWLEDGEMENTS

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